Infrared Auroral Emissions Driven by Resonant Electron Impact Excitation of NO Molecules

L. Campbell,[1] M. J. Brunger,[1] Z. Lj. Petrovic,[2] M. Jelisavcic,[3] R. Panajotovic,[3] and S. J. Buckman[3]

Received 25 November 2003; revised 28 March 2004; accepted 21 April 2004; published 25 May 2004.

[1] Although only a minor constituent of the earth's upper atmosphere, nitric oxide (NO) plays a major role in infrared auroral emissions due to radiation from vibrationally excited (NO*) states. The main process leading to the production of these excited molecules was thought to be chemiluminescence, whereby excited nitrogen atoms interact with oxygen molecules to form vibrationally excited nitric oxide (NO*) and atomic oxygen. Here we show evidence that a different production mechanism for NO*, due to low energy electron impact excitation of NO molecules, is responsible for more than 30% of the NO auroral emission near 5 μm. *INDEX TERMS:* 0310 Atmospheric Composition and Structure: Airglow and aurora; 0358 Atmospheric Composition and Structure: Thermosphere—energy deposition; 0360 Atmospheric Composition and Structure: Transmission and scattering of radiation. **Citation:** Campbell, L., M. J. Brunger, Z. Lj. Petrovic, M. Jelisavcic, R. Panajotovic, and S. J. Buckman (2004), Infrared Auroral Emissions Driven by Resonant Electron Impact Excitation of NO Molecules, *Geophys. Res. Lett.*, *31*, L10103, doi:10.1029/2003GL019151.

1. Introduction

[2] Mapping the intimate, and at times profound, connection between nanoscale atomic and molecular interactions and the macroscopic world in which we live is one of the outstanding successes of modern science. There are numerous examples of this, from gas lasers, to recent advances in the understanding of radiation damage in human cells [*Boudaiffa et al.*, 2000]. A significant number of these processes, particularly those based on discharge technology and atmospheric/astrophysical phenomena, are driven by electron-molecule impact and, in many cases, the nature of this interaction is profoundly dependent on the formation of intermediate, transient negative ion species which greatly enhance the reaction probability [e.g., *Boudaiffa et al.*, 2000]. Low energy electron collisions with nitric oxide are a further example of such resonant phenomena, and recent experiments [*Josic et al.*, 2001; *Jelisavcic et al.*, 2003] have quantified the dominant role that NO^- plays as an intermediary in the formation of vibrationally excited NO molecules. This negative ion complex only lives for the order of 10–100 femtoseconds and decays by electron emission, preferentially leaving the molecule in a vibrationally excited level. These measurements indicate that at low electron energies (1–3 eV), the vibrational excitation cross sections are enhanced by several orders of magnitude by the influence of the intermediate negative ion complex. When this new experimental data is included in existing atmospheric models of infrared auroral emissions, a new insight into the role of electron-driven processes in our upper atmosphere emerges.

[3] Earth's atmosphere is a complicated, dynamic system exhibiting both spatial and temporal dependence. Complex environments (e.g., the ionosphere and aurora under dayglow and nightglow) coexist and represent a considerable challenge in understanding their behaviour. Sophisticated computational packages have been developed, for example AURIC [*Strickland et al.*, 1999] and IZMIRAN [*Pavlov and Oyama*, 2000], in order to try and model and interpret these phenomena, with significant success being achieved. However, these previous descriptions could not have included the important quantitative information for the underlying excitation processes that has arisen in recent years, in particular the recent measurements for the low energy vibrational excitation processes. To this end we have used the accurate NO vibrational excitation cross sections which have arisen from the recent studies [*Josic et al.*, 2001; *Jelisavcic et al.*, 2003] to construct a new set of collision cross sections for NO which has been used, in conjunction with our suite of enhanced statistical equilibrium codes [L. Campbell et al., manuscript in preparation, 2004], to study two exemplar systems. These are the electron energy transfer rates (Q) for vibrational excitation of NO, which are crucial quantities in any description of the ionosphere [*Pavlov and Oyama*, 2000], and the production mechanisms for vibrationally excited NO under IBCII+ auroral conditions. These particular systems were targeted both for the transparency by which they link Angstrom-scale processes to the macroscopic behaviour of our atmosphere, and for their ability to elucidate the relative importance of electron-driven processes in atmospheric behaviour. This is particularly true in the latter case, where we shed new light on the origin of the observed auroral NO* fundamental lines near 5 μm.

2. Modelling Studies

[4] The modelling of such atmospheric phenomena is an extremely challenging task with many, often coupled, feedback mechanisms. The output from such modelling codes [*Pavlov and Oyama*, 2000] can, however, be directly compared to measured data, for example the time dependence of the electron temperature as a function of altitude,

[1]School of Chemistry, Physics and Earth Sciences, Flinders University, Adelaide, South Australia.
[2]Institute of Physics, Belgrade, Serbia and Montenegro.
[3]Atomic and Molecular Physics Laboratories, Research School of Physical Sciences and Engineering, Australian National University, Canberra, Australia.

0094-8276/04/2003GL019151$05.00

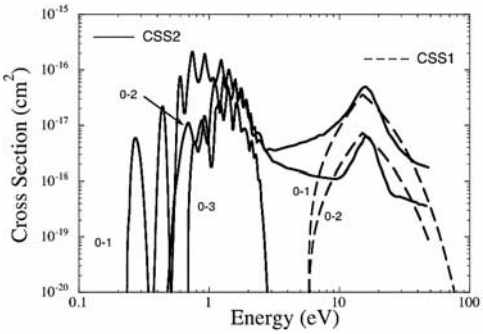

Figure 1. Collision cross section sets used in the present study (CSS2 – solid lines) for the 0–1, 0–2 and 0–3 vibrational modes of NO, compared with those (CSS1 – dashed lines) used in the Auroral model of *Cartwright et al.* [2000]. For clarity, the electronic excitation cross sections, which were common to both sets, are not shown. See color version of this figure in the HTML.

during geomagnetic storms. An important input to such codes are the electron cooling rates (L) due to electron-molecule collisions and it has been demonstrated [*Pavlov and Oyama*, 2000; *Pavlov*, 1998; *Prasad and Furman*, 1973], that collisions resulting in vibrational excitation are critical. The electron cooling rates depend sensitively upon factors such as molecular number density, electron temperature, electron density and electron energy transfer rates. The electron energy transfer rate for vibrational excitation from the ground state to some vibrational level ν is given by

$$Q_{0\nu} = E_\nu (8kT_e/\pi m_e)^{1/2} \int_0^\infty \sigma_{0\nu}(x) x e^{-x} dx \qquad (1)$$

where $x = {}^{E}/_{kT_e}$, k is Boltzmann's constant, E the electron energy, E_ν the vibrational excitation energy, m_e the mass of the electron, T_e the electron temperature and $\sigma_{0\nu}$ is the integral vibrational cross section (ICS) for electron impact excitation from the ground state to state ν. It follows that the total electron energy transfer rate for vibrational excitation is

$$Q_T = \sum_{\nu=1}^{N} Q_{0\nu} \qquad (2)$$

where N is the number of vibrational levels included in the model. In our case this is 3.

[5] Equation (1) explicitly links a macroscopic quantity describing ionospheric behaviour (Q and thus L) with a quantity ($\sigma_{0\nu}$) concerned with the angstrom-scale behaviour of the atmospheric electrons in collisions with NO molecules. We evaluate equation (1) numerically using two different cross section sets to describe the electron-NO interactions. The first cross section set (CSS1) is that used by *Cartwright et al.* [2000] in their earlier study of the electronic-vibrational behaviour of NO under auroral conditions. The second cross section set (CSS2) uses the same cross sections for electronic excitation as Cartwright et al., while the cross sections for ground state vibrational excitation are based on the recent absolute measurements [*Josic et al.*, 2001; *Jelisavcic et al.*, 2003]. These cross section sets are shown in Figure 1 and it is readily apparent that the main difference is the significant level of vibrational excitation in CSS2 at energies below 5 eV. This is due entirely to the enhanced scattering caused by the intermediate NO^- resonant state. The peak-like structure in the cross section below 5 eV is due to quasi-vibrational motion of the long-lived negative ions. These large magnitude, low energy features were not included in the cross section set of *Cartwright et al.* [2000] because, at that stage, the absolute values had not been determined. Indeed, the only prior estimate of the magnitude of these cross sections below 5 eV was that of *Spence and Schulz* [1971]. Their values were at least a factor of 20 smaller than those that we use here in CSS2.

3. Results and Discussion

[6] The results of the computation of Q_T as a function of T_e are given in Figure 2. The total electron energy transfer rate—that is, the energy transferred in electron-NO collisions—is significantly smaller when calculated with CSS1 than CSS2, particularly at low electron temperatures. This is a direct result of including the resonantly enhanced, low energy cross sections in CSS2. It is also interesting to note that when the present electron energy transfer rates for NO are compared to those calculated previously for N_2 [*Campbell et al.*, 2004] and O_2 [*Jones et al.*, 2003], we find that the NO rate for the F1-region of the ionosphere is an order of magnitude greater than the corresponding N_2 rate and 1.5 orders of magnitude larger than the corresponding O_2 rate. This is also demonstrated in Figure 2. That the O_2 curve is similar to that for NO at low electron temperatures is attributable to the fact that the scattering cross sections for O_2 are similarly enhanced by an O_2^- intermediary at energies below 1 eV. In the case of N_2 the vibrational scattering cross sections are also resonantly enhanced but at substantially higher energies (2–5 eV) and this is reflected by the kink in the N_2 curve at around T_e = 1500 K. Thus while the number density of NO is only a small fraction of that for N_2 and O_2, it appears that it is substantially more efficient in electron-energy transfer, and thus electron cooling, than either N_2 or O_2. This result again reflects the importance of the low energy NO cross sections in understanding general atmospheric behaviour.

[7] There have been few in situ atmospheric measurements for NO fundamental emissions (ν' to ν'-1). One of the more expansive was the IR rocket-borne interferometer investigation of *Espy et al.* [1988], who collected IR

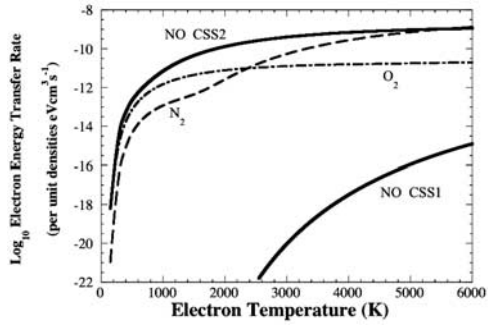

Figure 2. The electron energy transfer rates (per unit densities) for NO calculated using the two scattering cross sections sets, CSS1 and CSS2. Note the vertical axis is a log scale. Also shown, as dashed and dash-dot lines respectively, are the corresponding energy transfer rates for N_2 and O_2. See color version of this figure in the HTML.

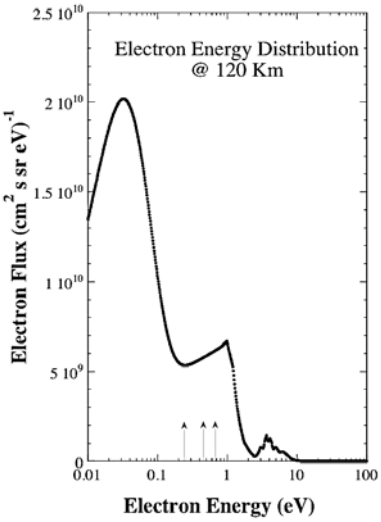

Figure 3. The electron energy distribution function used for the present study. The arrows indicate the threshold energies for the first three vibrational modes of the ground state of NO. See color version of this figure in the HTML.

emission data from an IBC II+ class aurora. Relatively strong NO emission lines were observed, in particular for NO(1,0), NO(2,1), NO(3,2), NO(4,3), NO(5,4), NO(6,5) and NO(7,6) radiation. *Espy et al.* ascribed the origin of these lines to the chemi-luminescent process:

$$N\left(^2D\right) + O_2 \rightarrow NO^*(\nu' = 1 - 12) + O. \tag{3}$$

In doing so Espy et al. apparently did not take into account possible contributions from electron-driven processes, even though *Cartwright et al.* [1971, 1972] had already demonstrated their general importance under auroral conditions for N_2 and O_2 respectively.

[8] In the present work these excitation mechanisms have been investigated using statistical equilibrium simulations which are based on the work of *Cartwright et al.* [2000, 1971, 1972]. The concept of statistical equilibrium was first developed by *Jefferies* [1968], and was originally coded in a meaningful way by Cartwright and colleagues in their studies on N_2 and O_2 under auroral conditions [*Cartwright et al.*, 1971, 1972]. Its principle of operation is conceptually quite straightforward [e.g., *Cartwright et al.*, 2000] in that for each possible energy level the code compares the population gain (due to electron-impact excitation and radiative transition into that level) with the loss (due to radiative transitions from that level, collisional quenching and pre-dissociation). An adjustment is made to the population of each energy level depending on the difference between the gain and loss mechanisms. This procedure is then repeated until the differences become negligible, i.e., a steady state is reached. Very recently the code has also been further enhanced to account for chemical processes in the atmosphere [*Campbell et al.*, 2004].

[9] Formally, the statistical equilibrium equation is written as:

$$k^{\alpha}_{\nu'0} + \sum_{\beta}\sum_{i} A^{\beta\alpha}_{i\nu'}\frac{n^{\beta}_i}{n^x_0} = \left[\sum_{i,j,l}\left(A^{\alpha j}_{\nu' i} + Q^{\alpha l}_{\nu'}\right)\right]\frac{n^{\alpha}_{\nu'}}{n^x_0} \tag{4}$$

where $A^{\beta\alpha}_{i\nu'}$ is the spontaneous transition probability from vibrational level i of state β to vibrational level ν' of state α, $\frac{n^{\beta}_i}{n^x_0}$ is the relative number density of vibrational level i of electronic-state β to those in the ground electronic-vibrational state n^x_0, $Q^{\alpha l}_{\nu'}$ is the quenching rate of vibrational level ν' of state α by species l and,

$$k^{\alpha}_{\nu'0} = n_e \int_0^{\infty} \mathrm{v}\sigma^{\alpha}_{\nu'0}(\mathrm{v}) f(\mathrm{v}) d\mathrm{v} \tag{5}$$

is the electron excitation rate of vibrational level ν' of state α from the ground electronic-vibrational state. Here $n_e f(\mathrm{v})$ is the auroral secondary electron distribution (see Figure 3), v is the electron velocity and $\sigma^{\alpha}_{\nu'0}$ is the rotationally averaged electron impact excitation cross section for the ν'^{th} vibrational level of state α. In the present study, relevant values for the $A^{\beta\alpha}_{i\nu'}$ and $Q^{\alpha l}_{\nu'}$ were taken from the work of *Cartwright et al.* [2000].

[10] The present simulation was carried out for an IBC II+ aurora, at an altitude of 120 km, for the photon emission rate as a function of wavelength for the NO(1,0), NO(2,1) and NO(3,2) fundamental lines. For these calculations the NO concentration was set at 8.2×10^8 cm^{-3}, a value that has been observed for the NO number density under IBC II+ conditions. The electron energy distribution function which was used was that from the work of *Campbell et al.* [2004] and this is shown in Figure 3. Full details of the altitude dependence of the distribution functions can be found in *Campbell et al.*, but we note that it is based on the work of *Lummerzheim and Lilenstein* [1994] and *Sharp and Hays* [1974]. Our analysis was conducted for both cross section sets, CSS1 and CSS2. Also included in this simulation, amongst other chemical reactions, was the chemiluminescent process represented by equation (3). The results of these simulations are presented in Figure 4 where we show the relative contributions from both chemiluminescent

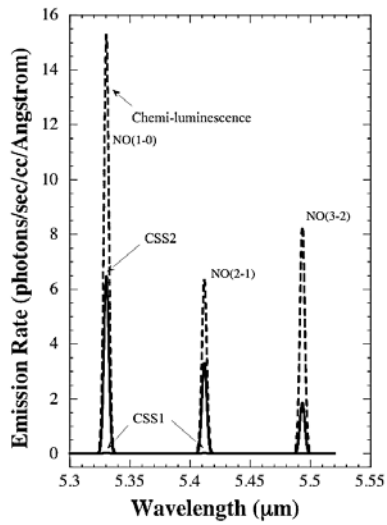

Figure 4. Photon emission rates due to chemiluminescence and vibrational excitation proceses for the (1, 0), (2, 1) and (3, 2) bands of the ground state of NO. Note that the rate calculated using CSS1 is very small, as indicated. See color version of this figure in the HTML.

and electron-driven processes to the photon emission rate for the lowest three NO lines. It is clear that the electron-driven emission rate, when calculated using CSS1, is a very small fraction (e.g., about 0.2% for the 1-0 line) of that originating from the chemiluminescent process. However, when the recently measured vibrational cross sections (CSS2) are employed, the electron-driven processes make a significant contribution, for each of the three lines, to the overall photon emission rate. For example, for the (2,1) line this amounts to more than 34%. We should also note that the radiation from the NO(1,0), (2,1) and (3,2) fundamental lines is found, in our model, to be strongly altitude dependent. For example for the (1,0) line, the contribution due to electron-driven processes has decreased to about 6.5% of the overall photon emission rate at an altitude of 150 km.

4. Conclusions

[11] The present work clearly indicates that the origin of the fundamental lines in the IR spectra of NO, under auroral conditions, is due to important contributions from *both* chemiluminescent *and* electron—driven effects. It is intriguing to note the events that lead to this conclusion. Figures 1 and 3 indicate the strong overlap that occurs between the resonant behaviour in the vibrational excitation cross sections at an energy of 0.5–2 eV, and a corresponding knee in the electron energy distribution function in the same energy region. It is exactly these electrons that become bound, with high probability, to the NO molecule for a short period of time and then detach themselves with a preference for leaving the molecule in a vibrationally excited state. We note that outside this energy region, and that of a higher-lying resonance at around 15 eV, the vibrational excitation cross section due to direct scattering processes is at least two orders of magnitude smaller. The significant role that electron driven processes play in the IR auroral emissions from NO is thus the result of a serendipitous convergence of molecular structure and the natural distribution of electrons in the upper atmosphere. It demonstrates beautifully how low energy molecular excitation on the angstrom size scale, and the femtosecond time scale, can drive processes occurring across hundreds of kilometres of the upper atmosphere.

[12] We anticipate that the next step in the analysis will be a quantitative comparison between the emission rates predicted by using the various (new and old) cross section sets and the experimental data of *Espy et al.* [1988].

[13] **Acknowledgments.** This work was supported, in part, by a Flinders University Small Grant and by the Australian Research Council. Z.Lj.P acknowledges the support of the Serbian Ministry of Science through program MNTRS 1478 and is grateful to Grzegorz Karwasz for his collaboration on the NO cross section determinations and for numerous useful discussions.

References

Boudaiffa, B., P. Clouthier, D. Hunting, M. Huels, and L. Sanche (2000), Resonant Formation of DNA Strand Breaks by Low Energy (3 to 20 eV) Electrons, *Science*, *287*, 1658.

Campbell, L., M. Brunger, D. Cartwright, and P. Teubner (2004), Production of Vibrationally Excited N_2 by Electron Impact, *Planet. Space. Sci*, in press.

Cartwright, D., S. Trajmar, and W. Williams (1971), Vibrational Population of the $A^3\,\Sigma_u^+$ and $B^3\Pi_g$ states of N_2 in Normal Auroras, *J. Geophys. Res.*, *76*, 8368.

Cartwright, D., S. Trajmar, and W. Williams (1972), The Excitation of O_2 in Auroras, *Ann. Geophys.*, *28*, 397.

Cartwright, D., M. Brunger, L. Campbell, B. Mojarrabi, and P. Teubner (2000), Nitric Oxide Excited Under Auroral Conditions: Excited State Densities and Band Emissions, *J. Geophys. Res.*, *105*(A9), 20,857–20,868.

Espy, P., C. Harris, A. Steed, J. Ulwick, R. Haycock, and R. Straka (1988), Rocketborne Interferometer Measurement of Infrared Auroral Spectra, *Planet. Space. Sci.*, *36*, 54.

Jefferies, J. (1968), *Spectral Line Formation*, pp. 110–134, Blaisdell Press, Waltham Mass., USA.

Jelisavcic, M., R. Panajotovic, and S. J. Buckman (2003), Absolute Cross Sections for Low Energy Electron Scattering from NO: The Role of Resonances in Elastic Scattering and Vibrational Excitation, *Phys. Rev. Lett.*, *90*, 20,3201.

Jones, D., L. Campbell, M. Bottema, and M. Brunger (2003), New Electron-Energy Transfer Rates for Vibrational Excitation of O_2, *New. Journ. Phys.*, *5*, 1.1.

Josic, L., T. Wroblewski, Z. Lj. Petrovic, J. Mechlinska-Drewko, and G. Karwasz (2001), Influence of resonant scattering on electron-swarm parameters in NO, *Chem. Phys. Lett.*, *350*, 318.

Lummerzheim, D., and J. Lilenstein (1994), Electron transport and energy degradation in the ionosphere: Evaluation of the numerical solution, comparison with laboratory experiments and auroral observations, *Ann. Geophysicae*, *12*, 1039.

Pavlov, A. (1998), New Electron Energy Transfer Rates for Vibrational Excitation of N2, *Ann. Geophysicae*, *16*, 176.

Pavlov, A., and K.-I. Oyama (2000), The Role of Vibrationally Excited Nitrogen and Oxygen Over Millstone Hill During 16–23 March, 1990, *Ann. Geophysicae*, *18*, 957.

Prasad, S., and D. Furman (1973), Electron Cooling by Molecular Oxygen, *J. Geophys. Res.*, *78*, 6701.

Sharp, W. E., and P. B. Hays (1974), Low-Energy Auroral Electrons, *J. Geophys. Res.*, *79*, 4319.

Spence, D., and G. Schulz (1971), Vibrational Excitation and Compound States in NO, *Phys. Rev. A.*, *3*, 1968.

Strickland, D., J. Bishop, J. Evans, T. Majeed, P. Shen, R. Cox, R. Link, and R. Huffman (1999), Atmospheric Ultraviolet Radiance Integrated Code (AURIC): Theory, software architecture, inputs and selected results, *J. Quan. Spectrosc. and Rad. Trans.*, *62*, 689.

M. J. Brunger and L. Campbell, School of Chemistry, Physics and Earth Sciences, Flinders University, GPO Box 2100, Adelaide 5001, South Australia.

S. J. Buckman, M. Jelisavcic, and R. Panajotovic, Atomic and Molecular Physics Laboratories, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia. (stephen.buckman@anu.edu.an)

Z. Lj. Petrovic, Institute of Physics, Pregrevica 118, 11080 Zemun, Belgrade, Serbia and Montenegro.